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MICROSTRUCTURES OF ANCIENT AND HISTORIC SILVER

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Abstract

The microstructures of silver-copper alloys from archaeological and historical contexts have been of particular interest since age-related changes at grain boundaries were first mooted as an indicator of antiquity and authenticity. Subsequent discussion has focused on how such structures might be reproduced by appropriate heat treatments, but there was only limited experimental investigation of these precipitation phenomena. A second strand of interest has been the embrittlement of archaeological silver by segregation of impurities to grain boundaries. More recently, industrial interest in silver-copper alloys has developed because of their use as solders and in electrical contacts, and a growing number of papers on sterling and other silver alloy microstructures are being published.

To interpret the microstructures of ancient and historic silver the key question is how to distinguish between the respective contributions of manufacture, age and the environment. This paper will describe and discuss a series of heat treatment experiments on wrought Britannia and Sterling silver and also on cast Sterling, the microstructure of cast silver being hitherto a rather neglected topic. The simple eutectic silver-copper system can exhibit a variety of precipitate morphologies and these have been characterised using optical microscopy, scanning and transmission electron microscopy, electron backscatter diffraction, and microhardness and nanoindenter testing. As a test case for discriminating between the effects of manufacture and age, a series of medieval Islamic silver coins with a range of mint technologies has been examined in detail and the results presented here. The data will also be used to highlight the limits within which age-related modifications of the microstructure can be expected to be observed.

Keywords

Silver-copper alloys, heat-treatment, supersaturation, precipitation, characterisation, ageing.

Introduction

In the arena of the cultural heritage, the opportunity for sampling artefacts for optical or electron microscopy has been in inverse proportion to the perceived intrinsic value of the material. Thus published microscopy of silver alloys is but a small proportion of that of copper- and iron-based alloys, while that for gold alloys is an even tinier fraction. What interest there has been has centred on the question of changes in microstructure at ambient temperature over archaeological time, first proposed by Schweizer and Meyers as a measure of authenticity (Schweizer and Meyers, 1978a; 1978b; 1979) and, later, on the embrittlement of ancient silver objects (e.g. Wanhill, et al., 1998). That changes do occur over time is shown by a recent study of the Gundestrup cauldron, a first century BC find from Denmark. The silver plates making up this vessel show modified grain boundaries in fully annealed sheets, but not in those with cold work; if the changes had occurred with the final heat treatment they would be in both. This study and others have also shown the usefulness of different microscopy techniques, for example electron backscatter diffraction (EBSD) has also been explored in relation to ancient silver (Wanhill et al., 2008; Northover and Northover, 2012).

In recent years, the structure and properties of silver-copper have again become a subject of industrial and academic interest and a new literature on the precipitation and age-hardening behaviour of these alloys is developing. The project described here is designed to document the transformations induced by heat treatment in wrought Britannia silver and wrought and cast Sterling silver for comparison with the microstructures of ancient and historic silver artefacts. The initial objective is to explore the mint technologies used in the production of a variety of medieval Islamic silver coins and to distinguish the microstructural features created during manufacture from those created by ageing at ambient temperature over archaeological time. The structures are studied using optical (OM) and scanning electron microscopy (SEM), including at high resolution, electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), and microhardness and nanoindenter testing. Besides an annotated library of micrographs, quantitative data have been created to measure the progress of transformation with time and temperature. The microstructures observed in the experimental material can also be subtracted from those of the coins and other artefacts to identify the effects of ageing at ambient temperature.

Sample material and preparation

For the evaluation of wrought alloys, coupons 10 mm to 15 mm square were cut from Britannia (95.84% silver, 4.16% copper) and Sterling (92.5% silver, 7.5% copper) strip. The samples were homogenised for 1 hour at 700 °C (Britannia) and 760 °C (Sterling) and then rapidly quenched in water. The subsequent heat treatments are listed by time and temperature in Table 1. Cast Sterling silver samples were cut from sprue from recent sculpture cast by Pangolin Editions. The Islamic coins studied were worn specimens bought for the project and then sectioned for metallography and microanalysis. All samples were prepared for optical and scanning electron microscopy and microhardness testing by hot mounting in a carbon-filled thermosetting resin followed by grinding and polishing to a 1 µm diamond finish. Etching was with ammoniacal hydrogen peroxide, the optimal proportions being 3 ml 30% hydrogen peroxide, 17-20 ml ammonium hydroxide and 10 ml distilled water. Alternate cycles of polishing and etching, ending in a light etch to minimise relief, followed by carbon coating, served to prepare the samples for EBSD. TEM samples were cut from the polished and etched coupons using a focused ion beam (FIB) instrument.

Britannia	Sterling
700 °C for 20 mins	760 °C for 2 hours
700 °C for 20 mins then 650°C for 1 hour	720 °C for 30 mins
700 °C for 20 mins then 600°C for 1 hour	760 °C for 2 hours then 600°C for 1 hour
700 °C for 20 mins then 550°C for 1 hour	760 °C for 2 hours then 500°C for 1 hour
700 °C for 20 mins then 500°C for 1 hour	760 °C for 2 hours then 450°C for 1 hour
700 °C for 20 mins then 450°C for 1 hour	760 °C for 2 hours then 400°C for 1 hour
700 °C for 20 mins then 400°C for 1 hour	760 °C for 2 hours then 350°C for 1 hour
700 °C for 20 mins then 350°C for 1 hour	760 °C for 2 hours then 300°C for 1 hour
700 °C for 20 mins then 300°C for 1 hour	760 °C for 2 hours then 250°C for 1 hour
700 °C for 20 mins then 250°C for 1 hour	760 °C for 2 hours then 200°C for 1 hour
700 °C for 20 mins then 200°C for 1 hour	760 °C for 2 hours then 150°C for 1 hour
700 °C for 20 mins then 150°C for 1 hour	760 °C for 2 hours then 250°C for 2 hours
700 °C for 20 mins then 100°C for 1 hour	760 °C for 2 hours then 250°C for 3 hours
700 °C for 20 mins then 600°C for 24 hours	
700 °C for 20 mins then 500°C for 24 hours	
700 °C for 20 mins then 500°C for 24 hours then furnace-cooled	
700 °C for 20 mins then 400°C for 24 hours	
700 °C for 20 mins then 200°C for 24 hours	
700 °C for 20 mins then 200°C for 72 hours	
700 °C for 20 mins then 100°C for 840 hours	
800 °C for 1 hour	
800 °C for 1 hour then air-cooled	
800 °C for 1 hour then furnace-cooled	

Table 1. Summary of heat treatments used for Britannia and Sterling silver.

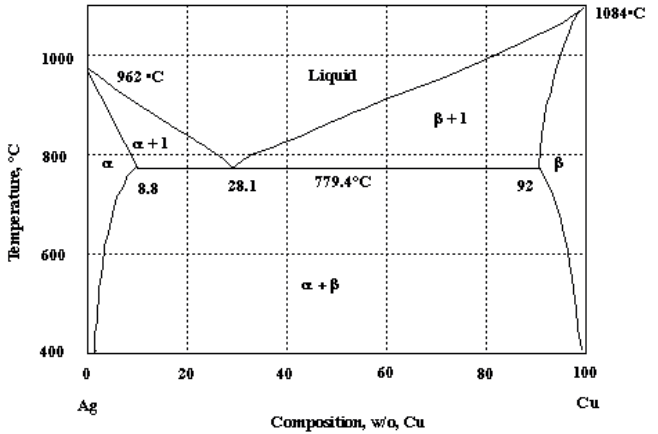


Figure 1: Equilibrium phase diagram for the silver-copper system.

The silver-copper system

The silver-copper alloy system (Fig. 1) is a simple eutectic. The eutectic temperature is 779.1 °C (Subramanian and Perepezko, 1993) and the eutectic composition is 28.41 wt% copper. The maximum solid solubility of copper in silver at the eutectic temperature is 8.27 wt%; the maximum solid solubility at room temperature is not known with certainty but is significantly below 1 wt%. It is the resultant supersaturation of copper in metastable solid solution in silver-copper alloys quenched from high temperature which is the primary factor in the precipitation phenomena described in this paper.

Precipitation in wrought silver alloys

The increase in copper content between Britannia and Sterling silver has a major effect on the transformations induced by a given heat treatment and the visual appearance of the microstructures. In each case the respective homogenisation treatment followed by quenching produced a recrystallised grain structure with no visible copper-rich phase (Fig. 2a), although great care had to be taken with the Sterling silver coupons to produce a rapid enough quench. When the homogenised samples were subsequently heat treated, a visibly transformed structure occurred in some cases. The proportion of the microstructure that was transformed was affected by various factors including the copper content of the alloy and the annealing time and temperature. The effect of the copper content on the amount transformed is illustrated by Figs. 2b and 2c comparing the microstructures of Britannia and Sterling silver annealed for 1 hour at 300 °C. It has previously been established that the amount transformed increases as the duration of the annealing treatment increases.

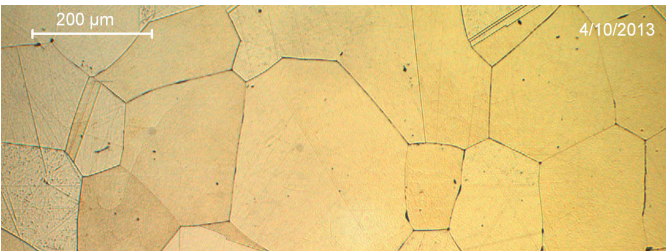


Figure 2a: Sterling silver strip homogenised for 2 hours at 760 °C.

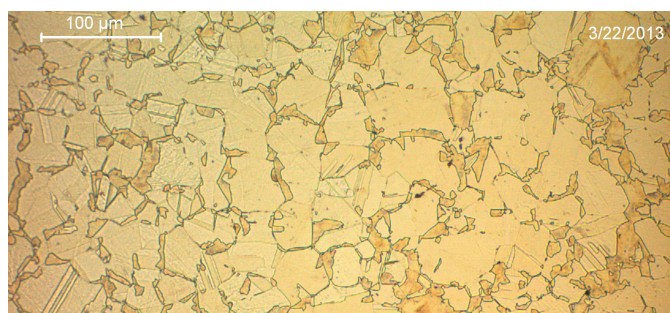


Figure 2b: Microstructure of Britannia silver homogenised for 20 minutes at 700 °C and then annealed for 1 hour at 300 °C.

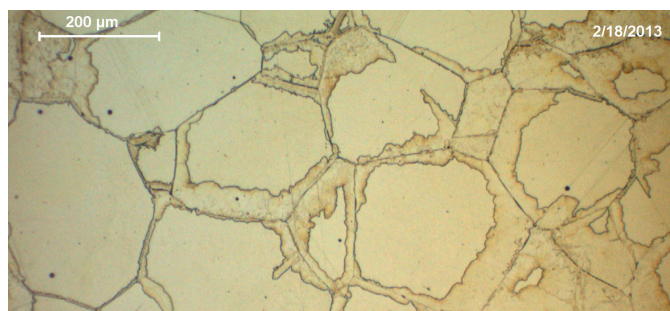


Figure 2c: Microstructure of Sterling silver homogenised for 2 hours at 760 °C and then annealed for 1 hour at 300 °C.

To investigate the effect of temperature, a point counting method with a grid of 11 x 16 points was used to measure the percentage of the microstructure visibly transformed in both Sterling and Britannia samples following a series of heat treatments for 1 hour at different temperatures. The results are presented graphically in Figs. 3a and 3b. It can be seen that the results are somewhat sparse at higher temperatures as it became difficult to distinguish the transformed regions. It is proposed that variation in the measurements obtained from different sets of Sterling samples (where a set refers to a batch of samples that were homogenised and quenched together) is due to small variations in quenching rate which have been shown to affect the transformation. These transformed regions are regions in which discontinuous precipitation has occurred. The growth morphologies that have been observed are typical of discontinuous precipitation, for example that shown in Fig. 4. This morphology is a typical structure observed in historic artefacts. The structure within regions of discontinuous precipitation is that of copper precipitate rods of varying sizes and orientations. This has been observed using higher magnification secondary electron and back-scattered electron imaging.

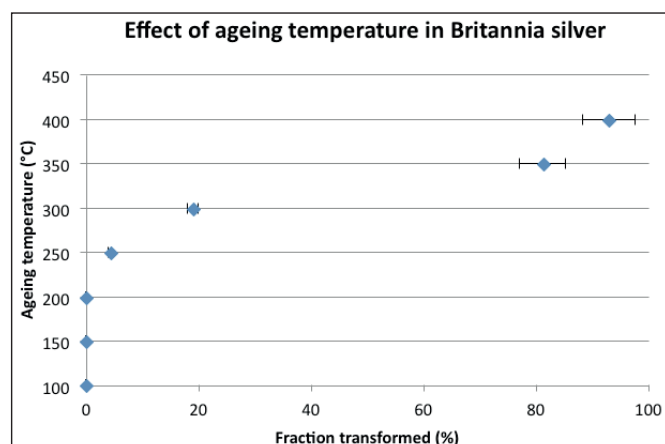


Figure 3a: Secondary electron image of Britannia silver homogenised at 800 °C for 60 minutes then air-cooled.

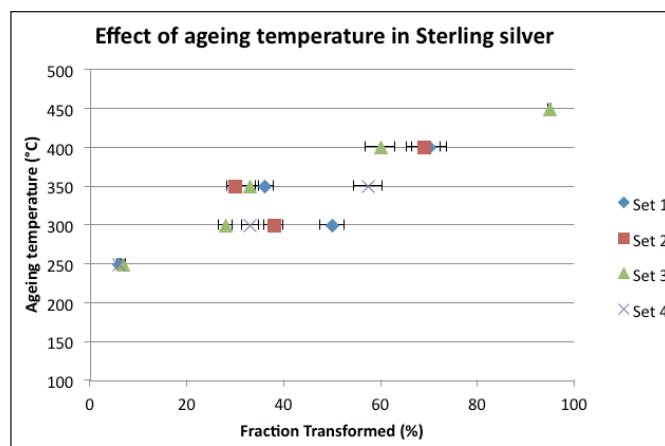


Figure 3b: Fraction visibly transformed versus ageing temperature for Britannia silver, homogenised and annealed for 1 hour.

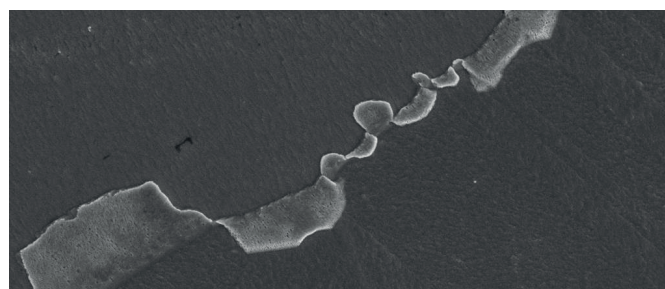


Figure 4: Fraction visibly transformed versus ageing temperature for Sterling silver, homogenised and annealed for 1 hour.

Continuous precipitation has also been observed in the wrought Britannia alloys, both on its own and in combination with discontinuous precipitation. It becomes visible at higher annealing temperatures and two different morphologies have been observed as shown in Figs. 5a and 5b. Both morphologies of continuous precipitation are more prevalent in samples which have been cooled at slower rates rather than quenched, while the criss-cross morphology in Fig. 5b has

been observed only in such samples. These morphologies have previously been observed at lower magnifications (e.g. Jones et al., 1942; Gayler and Carrington, 1947). The criss-cross morphology has also been observed in an historic artefact, a large casting in a Ag-Cu alloy. This is consistent with it being formed during manufacture as the cooling of a large object from high temperatures after casting will, by virtue of its size, be slow.

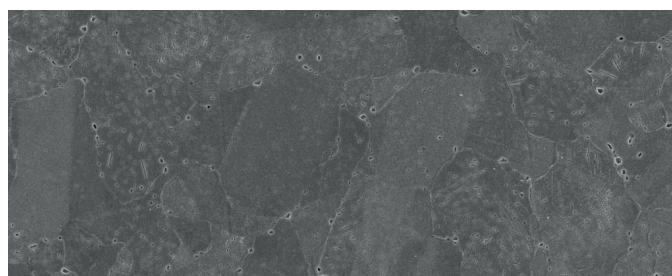


Figure 5a: Secondary electron image of Britannia silver homogenised for 20 minutes at 700 °C, annealed for 24 hours at 500 °C, then furnace cooled.

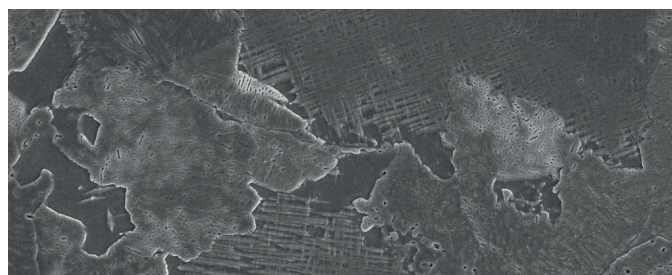


Figure 5b: Secondary electron image of Britannia silver homogenised for 1 hour at 800 °C, then furnace cooled.

These observations suggest that there are two competing processes taking place; continuous precipitation and discontinuous precipitation. Microhardness and nanoindentation measurements provide a further insight into the nature of these different regions of precipitation. There is a significant difference in hardness between visibly transformed and untransformed regions within each sample. Also, in certain samples where a variation in structure (or scale of structure) is visible, there is a corresponding variation in hardness. The measurements were performed using a Wilson Instruments 402MVD hardness tester with a Vickers indenter with a load of 10 g Fig. 6a shows a sample of Britannia silver in which such a difference is visible. The corresponding hardness data from three indents in each type of structure (Table 2) show that the visibly coarser (centre) part of the grain is considerably softer than the rest of the transformed region.

Region type	Average hardness (HV)
Transformed (edge by grain boundary)	118 ± 3.6
Transformed (centre by untransformed region)	175 ± 6.7
Untransformed	185 ± 5.8

Table 2: Variation in hardness with transformation.

The results of a more comprehensive hardness survey on the series of Sterling silver samples annealed at various temperatures for 1 hour are shown in Fig. 6b. A sudden increase in the hardness of the region, identified optically as untransformed, can be seen between the sample annealed at 200 °C and the one annealed at 250 °C. This corresponds to the annealing temperature at which a separate visibly transformed region is formed. The hardnesses of both untransformed and transformed regions gradually decrease from the sample annealed at 250 °C onwards. The decrease in hardness of the transformed regions can be explained by a visible increase in the coarseness of the precipitates within the regions. A possible explanation for the initial gradual increase and subsequent sudden discrete change in hardness of the visibly untransformed region is the formation of initially coherent zones followed by continuous precipitation to provide a hardening effect as proposed by Scharfenberger et al. (1972) and Leo, (1972). Such continuous precipitation has been seen by TEM in the present study in an ancient Ag-12Cu sample, but is too small to be seen at the magnifications used so far in examining the Sterling or Britannia silvers. The subsequent gradual decrease in hardening is attributed to over-coarsening of the precipitates.

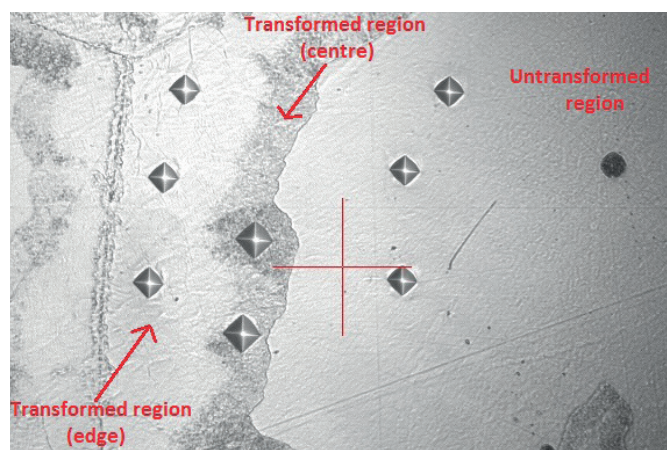


Figure 6a: Microhardness indents in Sterling silver homogenised for 2 hours at 760 °C, then annealed for 1 hour at 350 °C.

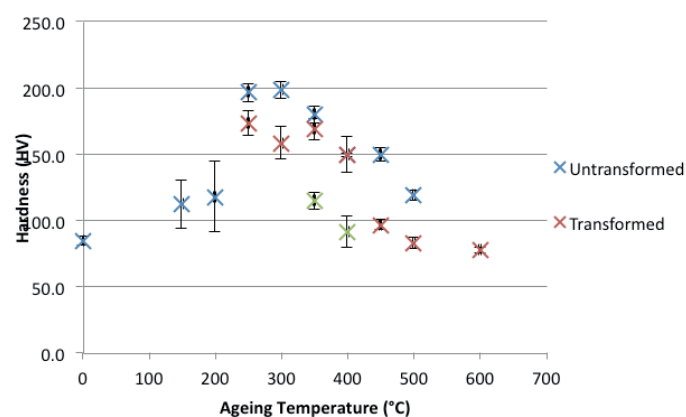


Figure 6b: Microhardness values for transformed and untransformed regions of homogenised and annealed Sterling silver.

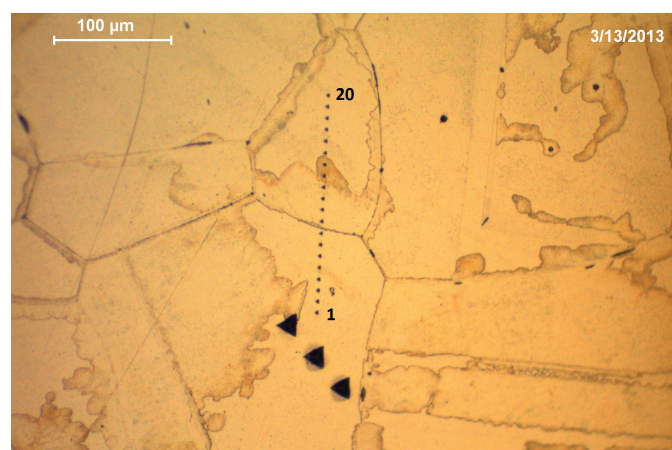


Figure 7a: Microhardness indents in Sterling silver homogenised for 2 hours at 760 °C, then annealed for 1 hour at 350 °C.

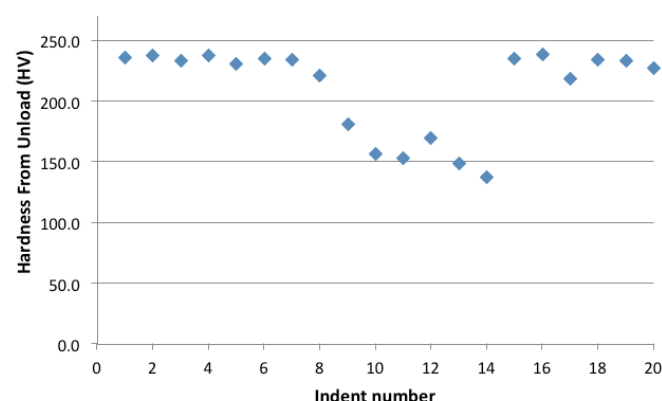


Figure 7b. Microhardness values for transformed and untransformed regions of homogenised and annealed Sterling silver.

Nanoindentation, which can fit more indents into a given region, has been applied to investigate the hardness variation in the transformed region in more detail. A Nanoindenter (MTS Instruments) with a Berkovich tip was used, indenting to a depth of 500 nm. The hardness results given here are those measured during unloading, as these are the closest in type to those calculated using the microhardness indenter. Fig. 7a shows a line of indentations made across a transformed region and into an untransformed region on each side. The corresponding hardness graph (Fig. 7b) shows a change in hardness across the transformed region which could suggest a gradual change in the coarseness of precipitation. This technique has been taken further to form arrays of indents from which hardness contour maps can be created and matched to the optical image.

The microstructures can also be further analysed using electron backscatter diffraction (EBSD). This was first applied to archaeological silver in the study of the Gundestrup cauldron referred to above (Wanhill et al., 2008). This method is very sensitive to surface perfection and determines the crystallographic orientation of the metal at each point in a raster to produce maps of grain orientations, high and low angle boundaries, twin and coincident site lattice boundaries

and elastic and plastic strains. An example from a Sterling silver sample homogenised for 2 hours at 760 °C and then annealed for 1 hour at 350 °C is given in Fig. 8. These maps show the crystallographic orientation of the transformed regions, the presence of strain and twin boundaries within them, and that they are bounded at the advancing interface by a coincident site lattice boundary. They also suggest that when there is a second stage of transformation this may be of a new orientation.

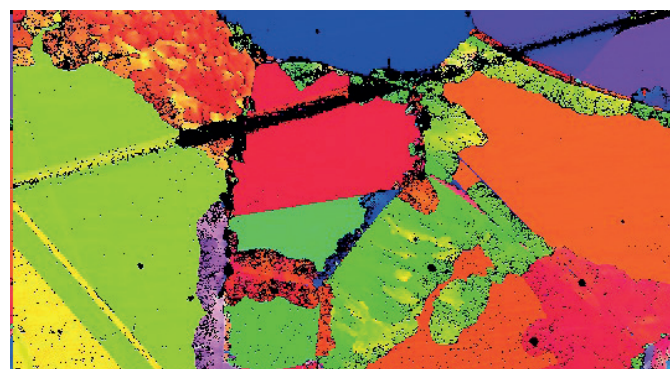


Figure 8: Inverse pole figure map of a Sterling silver sample homogenised for 2 hours at 760 °C and then annealed for 1 hour at 350 °C.

Microstructure of cast silver

Cast microstructures are very much in a minority in the corpus of published silver-copper alloy microstructures from archaeological and silver artefacts. Considering hypereutectic alloys only, very many of the samples show extensive discontinuous precipitation of copper across the silver matrix, as well as the interdendritic silver-copper eutectic. Other features of the microstructures are an oxidised surface zone (Fig. 9a) and twins (Fig. 9b). It was thought possible that these were the result of exposure of the object to fire, and to test this, pristine samples of sprue from large and small Sterling silver sculptures cast in normal atmospheric conditions or under vacuum were examined. In all cases some precipitation was observed, it being rather less abundant in the most rapidly cooled section. It is proposed that this coarse cellular precipitate forms during cooling from the solidus temperature down to 300-400°C. Also, in all cases an oxidised surface zone was observed as well as twins.

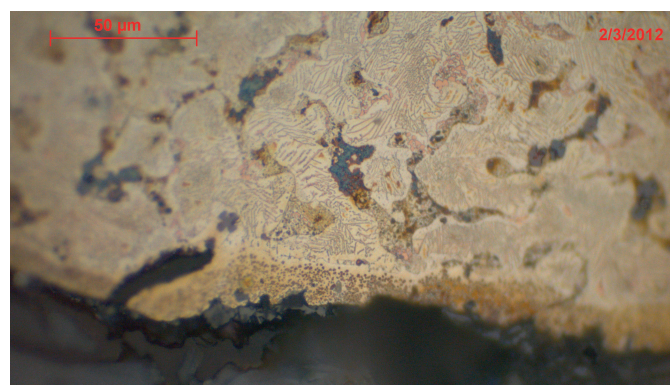


Figure 9a: Microstructure of a figure of an ibex cast in an Ag-14% Cu alloy, Achaemenid period.

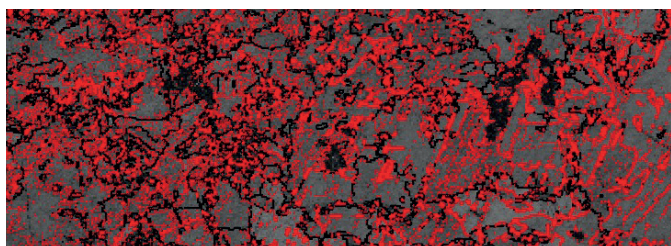


Figure 9b: Band contrast and grain boundary EBSD map of Sterling silver sprue: twin boundaries are red, grain boundaries black (sample courtesy of Pangolin Editions).

Identifying the grain boundaries in a cast silver sample is not easy when so much is obscured by precipitation. To overcome this, selected samples have been examined with EBSD. This has helped greatly to clarify the structure, especially where possible age-related changes have occurred at grain boundaries, although so far this has not often been observed. We believe that discontinuous precipitation can develop at grain boundaries during cooling but also at ambient temperature over archaeological time. Examples of both are currently being explored and will be published in detail elsewhere.

Microstructure of Islamic silver coins

In contrast to the West where silver coins had been struck from hammered sheet since at least the 9th century AD, medieval Islamic silver coins continued the Roman tradition of using cast blanks, flattened and heat-treated to a varying degree. The coins studied in this project range in date from the 9th to the 16th centuries AD, and in copper content from nearly fine silver to base silver-copper-lead alloys (Ilisch, et al., 2003). The coinages selected for discussion here are presented in order of increasing copper content. Ten coins of the central Asian Timurid dynasty (1370-1507) contained 0.3-4.0% copper. All show a homogenised, fully recrystallised structure with no visible cold work; the coins are thin and may have been through more than one cycle of cold work and annealing. Among these coins it is only those with >3.0% copper that show modified grain boundaries (e.g. Fig. 10) with a structure similar to that observed in homogenised and annealed silver in the Gundestrup cauldron (100 BC) and in silver vessels from Troy II (Northover and Northover, 2012). The structure is also similar to that developed in air-cooled Britannia silver. With similar structures developed over such a long period it is very difficult to say exactly what the contribution of ageing is.

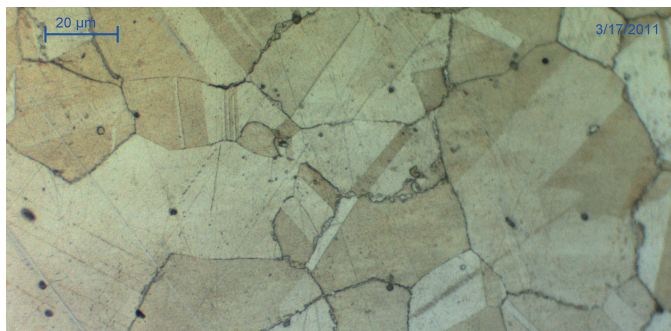


Figure 10: Timurid silver dirham, 15th century AD, 3.6% copper.

Coins were struck at the Umayyad mint at Wasit, Iraq during the period 708-741 AD (al-Saa'd, 1999), starting with a 5.6-6.6% copper, decreasing soon after to 3.4-4.2%, and moving to almost fine silver around 730 AD. The example shown in Figure 11a has a structure with similarities to those of the Britannia and Sterling samples annealed for 1 hour at 300 °C. The absence of segregation indicates that this coin was homogenised before further working of the blank and it could then have been annealed for a short time at a lower temperature, almost certainly above 300 °C, sufficient to produce secondary coarsening of the precipitate. Possibly a higher annealing temperature led to much more extensive coarse precipitates in another coin of the same issue (Fig. 11b). A future analysis with EBSD will resolve the crystallography.

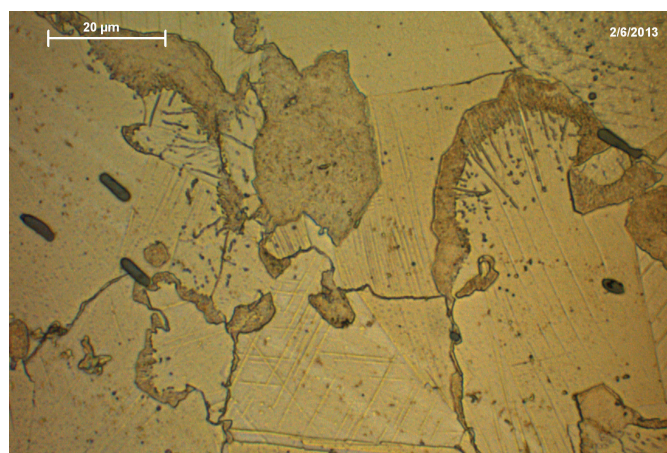


Figure 11a: Umayyad silver dirham, Wasit mint, 8th century AD, 5.1% copper.

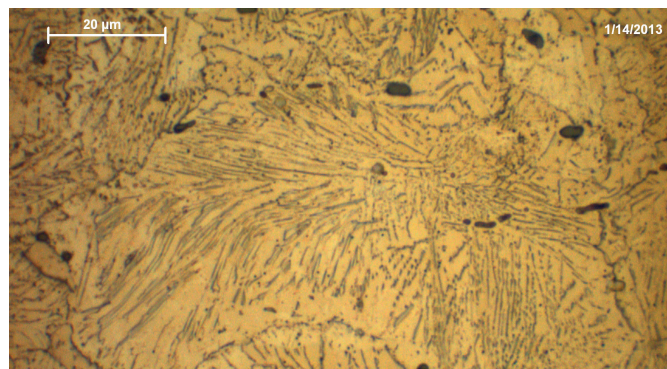


Figure 11b: Umayyad silver dirham, Wasit mint, 8th century AD, 4.4% copper.

The coins of the Samanid dynasty, ruling in central Asia from 819 AD to 999 AD, exhibit a very different approach to the preparation of the blanks. The coins analysed here spread from 4.4% to 14.6% copper, have a very thick oxidised surface zone and very extensive, coarse cellular precipitation with no trace of recrystallisation (Fig. 12a). Some coins, though, have a more complex structure with areas of both fine and coarse precipitation, possibly the result of two cycles of heating (Fig. 12b). One interpretation of the structure is that the blanks were flattened at hot working

temperature (say 600-700 °C), air cooled and, possibly, reheated to be hot struck. Hot striking of silver copper alloy coins is unusual because of the problem of firestain and it is noticeable that these coins still have firestained surfaces; there is at least one reference in a medieval treatise to hot striking but it does not mention where it might have been practised.

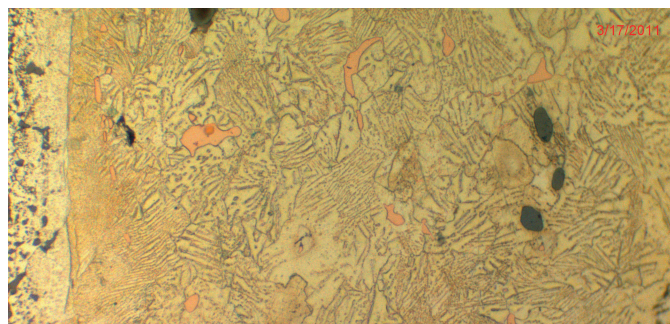


Figure 12a: Samanid silver dirham, 10th century AD, 6.3% copper.

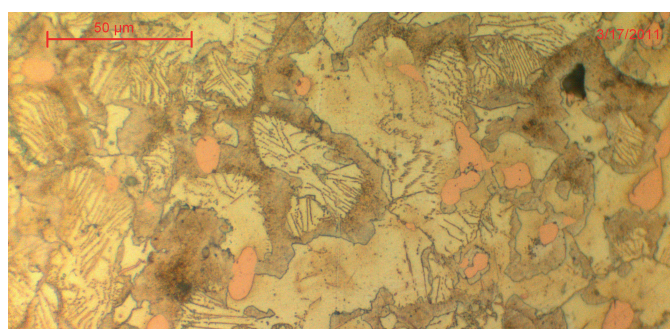


Figure 12b: Samanid silver dirham, 10th century AD, 9.1% copper.

A final contrast in both alloy and technology is offered by the Ghaznavid coinage, the Ghaznavids being the successors to the Samanids, and their rule lasted in some areas until 1186. They used copper-silver-lead alloys which are very heterogeneous but typical compositions are 30% Cu, 50% Ag, 20% Pb and 60% Cu, 35% Ag, 5% Pb. The microstructures present a considerable challenge to the metallographer but they do appear to have been cast close to their finished size and have received very little alteration before striking (Fig. 13).

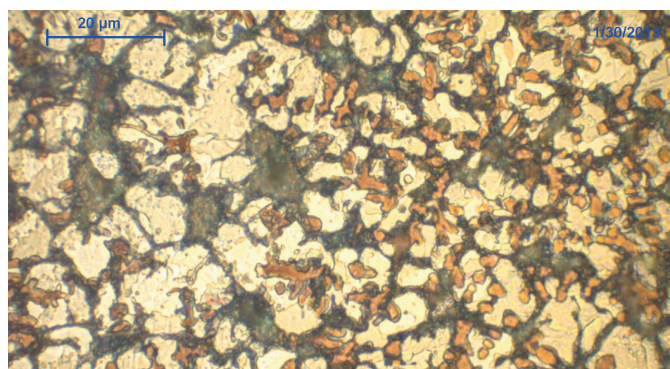


Figure 13: Ghaznavid silver dirham 12th century AD, 53% silver, 20% copper, 27% lead.

Discussion and identifying age-related changes

We have shown that the coins examined in this project exhibit a variety of precipitation behaviours dependent on mint technology. We have also shown, by comparing these microstructures with those created experimentally in Britannia and Sterling silver, that they can be explained solely in terms of thermal and mechanical treatments during their production. On the other hand, it is also clear, for example from the published work on the Gundestrup cauldron, that age-related changes at grain boundaries do occur in archaeological silver. The changes are clearest in alloys with 3-4 % copper, but the extent of the alteration is much the same for objects almost 4,000 years apart in age. We must therefore conclude that, at present, we have very great difficulty in separating the effects of ageing at ambient temperature over archaeological time from those induced during manufacture. However, the research presented here does point out two approaches for the way ahead. The first is to employ additional metallographic techniques and, in this context, microhardness testing and EBSD have both proved invaluable. The second is to increase the spatial resolution we use both in microscopy, with high resolution scanning electron microscopy and transmission electron microscopy, and in microanalysis, with scanning transmission electron microscopy and high resolution scanning Auger microscopy, so that we can analyse individual precipitates and their surrounding matrix. It may be that the silver content of the copper precipitates and the residual supersaturation in the silver vary with ageing temperature and so might provide a method of identifying ageing at ambient temperature. Optical microscopy alone is not enough.

Materials

Britannia silver and Sterling silver strip 15 mm wide x 2 mm thick for samples, Sterling silver sprue, by courtesy of Rungwe Kingdon, Pangolin Editions, Unit 8B, Chalford Industrial Estate, Chalford, Gloucestershire, GL6 8NT, United Kingdom.

Silicon carbide grinding papers from P600 to P4000 grades and 6 µm and 1µm monocrystalline diamond suspension in water: MetPrep Limited, Curriers Close, Charter Avenue, Coventry, Warwickshire, CV4 8AW, United Kingdom.

DP-Floc and DP-Nap polishing cloths: Struers Ltd, Unit 11 Evolution @ the AMP, Whittle Way, Catcliffe, Rotherham, S60 5BL, United Kingdom.

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